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Performance of Micelle-Clay Filters for Removing Pollutants and Bacteria from Tertiary Treated Wastewater

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Abstract: Filters filled with a micelle-clay complex mixed with sand were employed to investigate their purification capability of tertiary treated wastewater with loose UF-membranes. The UF membrane was hollow fiber with a molecular weight cutoff of 100 kD. The complex was prepared from the organic cation octadecyltrimethylammonium (ODTMA) and the negatively charged clay-mineral, montmorillonite. This complex has a very large surface area, which includes large hydrophobic domains and is positively charged, about half of the cation exchange capacity of the clay. Two sets of filtration experiments were carried out at flow rates of 1.2 and 50 mL/min, which correspond to flow velocities of 3.7 and 153 cm/h, respectively. In the first case, after a passage of 1 L, the turbidity, total suspended solids (TSS), fecal coliforms (FC), and total coliforms (TC) were reduced to zero from 14 NTU, 6 ppm, 350 and 10,000 counts per 100 mL, respectively. In the second case, the numbers of FC and TC were reduced from 50,000/100 mL to zero after the passage of 14 L. The values of COD and BOD were reduced several-fold. The conclusion is that the incorporation of micelle-clay filters in the sewage treatment system with loose tertiary capability is promising and warrants larger scale experiments for optimization of the overall system.

Key words: Clay-micelle complex, wastewater treatment, chemical oxygen demand, biological oxygen demand, microbial removal.

1. Introduction

In countries where fresh water is abundant, treatment of wastewater is performed to sustain and protect the environment from pollution. Treatment of wastewater enables to find alternative sources for fresh water, thus overcoming in part the increased scarcity of water in dry regions. The level of treatment is still a controversial issue. Quite a few countries are moving rapidly towards advanced treatment by which wastewater approaches fresh water quality, thus protecting the soil and aquifers from pollution [1, 2]. The major unit operations in wastewater treatment include the removal of suspended solids (TSS), dissolved solids (TDS), chemical oxygen demand (COD), biological oxygen demand (BOD), and pathogens. Usually suspended solids are removed by filtration methods ranging from sand to membranes with nano scale pores. Pathogens are removed by chlorination, ozonation, UV-disinfection [3, 4], or membrane filtration with less than 20 kD cutoff filters.

Recently, recognizing that bacterial cell surfaces

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possess net negative electrostatic charge by virtue of ionized phosphoryl and carboxylate substituents on outer cell envelope macromolecules which are exposed to the extracellular environment [5], adsorption on modified solid surfaces with positive charge centers was investigated towards the removal of microorganisms [6-10]. Such surfaces may also be useful in removing heavy metals which exist in anionic complexes, e.g., chromate, or arsenate, whereas negatively charged surfaces, such as the clay-mineral montmorillonite can remove heavy metals in cationic forms [11-14].

Al-Quds University wastewater treatment plant collects a mixture of black (from toilets), gray (from showers and sinks), and storm water, as well as waste water (from certain laboratories). The treatment plant consists of a primary treatment (two stage primary settling basin), and secondary treatment (activated sludge with a hydraulic retention time of 16-20 h, followed by coagulation and chlorination). Then the secondary effluent is introduced to a sand filter before entering the ultrafiltration membrane, which consists of a UF hollow fiber (HF) with 100 kD cutoff filters as pre polishing stage for the UF spiral wound with 20 kD cutoff filters. The spiral wound stage produces good water quality with less than 20 ppm BOD and less than 30 ppm TSS and free from bacteria, which makes the water suitable for non restricted irrigation. After ultrafiltration process, the effluent is filtered by activated carbon column followed by reverse osmosis (advanced treatment). Then a blend of UF effluent and effluents of reverse osmosis with salt content similar to that of fresh water are used for irrigation, thus sustaining the soil from deterioration due to salt buildup. It is worth noting that before the installation of ultra filtration with hollow fiber membrane, the spiral wound membranes had suffered severely from fouling which rendered this process to be expensive and not feasible. This fouling was mostly eliminated and thus the operation of the system improved significantly with the introduction of the HF unit. We tested whether introducing a clay-micelle complex filter within this system would further improve the overall process and would reduce the operational as well as the equipment cost drastically for this advanced system while preserving water quality.

We focus here on presenting a relatively novel means for removal of micropollutants and microorganisms from water using a micelle-clay sorbent. The micelle-clay composite which was used in this study is positively charged, has large surface area and includes large hydrophobic domains. It was shown by X-ray diffraction, electron microscopy and adsorption experiments that the material characteristics of the micelle-clay complex are different from those of an organo-clay complex, which are formed by adsorption of the same organic cation ODTMA (Octadecyltrimethylammonium) as monomers [15]. Micelle-clay composites have already been proven useful in the removal of about 20 neutral and anionic pollutants [16-18].

In this study we present some results of investigations of the efficiency of filters based on a micelle-clay complex towards polishing tertiary treated wastewater generated from ultrafitration plants using hollow fiber membranes with 100 kD cutoff filters. The filtration process was adopted to monitor the efficiency of the complex towards removing total suspended solids (TSS), turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), total bacteria count, total coliforms and fecal coliforms. This study is the first stage in a comprehensive evaluation of how micelle-clay complexes can be incorporated in a multi-stage procedure of treatment of waste water.

2. Experiment

2.1 Materials

The clay used was Wyoming Na-montmorillonite SWy-2 obtained from Steetley Bentonite & Absorbents (Nottinghamshire, UK). Quartz sand (grain size 0.8-1.5 mm) was purchased from Shoshani

& Weinstein (Israel). Octadecyltrimethylammonium (ODTMA)-bromide was obtained from Sigma Aldrich. Sulfuric acid (H_2SO_4: 95-97%, MERCK, 1.00731, Germany), potassium dichromate ($K_2Cr_2O_7$, Sigma, P5271, USA). Silver sulfate (Ag_2SO_4, Sigma, S-7638, USA). Mercury (II) sulfate ($HgSO_4$, Riedel-de Haen, 31013, Germany). De-ionized water was used to prepare all solutions. Microbiology growth media were obtained from Difco, USA (213000, 273620, and 267720 for total plate count, total coliform, and fecal coliform count, respectively).

2.2 Instruments

COD was determined spectrophotometrically using UV-visible spectrophotometer (Perkin Elmer Lambda 10). Dissolved oxygen was measured using Oxi-meter with water bath (WTW-Inolab). Electric conductivity (EC) was measured using pH-EC-TDS meter (HI 9812, Hanna instruments). Turbidity and total suspended solids were measured using HACH DR\2010 Portable Data logging Spectrophotometer. Total coliform and fecal coliform tests were determined using Millipore filtration system (Millipore pump coupled with stainless steel autoclaved funnel). 0.45 μm sterile cellulose nitrate filters were used (Cat. #11406-47-ACN, Sartorius Stedim Biotech, Germany). Total microbial count was determined by pour plate method after serial dilutions.

2.3 Methods

Micelle-clay complex preparation: The complex was prepared as described in previous investigations [15, 16], but with some modifications. Briefly, the micelle-clay complex was prepared by stirring 12 mM of ODTMA with 10 g/L clay for 24 h. Under these conditions most of ODTMA was in micellar form and most of the micelles as well as remaining monomers were adsorbed by the clay (> 99%) as previously determined by elemental analysis. Suspensions were centrifuged for 20 min at 15,000 g, supernatants were discarded, and the complex was lyophilized.

COD, BOD, turbidity, total suspended solids and microbial counts were determined using standard procedures [19].

Wastewater treatment: tertiary waste water treatment plant at Al-Quds University (Palestine) was used to obtain the UF permeates using hollow fiber membranes as described in detail in a recently published work [20]. Briefly, the wastewater treatment plant at Al-Quds University consists of a primary treatment unit (two stage primary settling basin), a secondary treatment unit (activated sludge with a hydraulic retention time of 16-20 h, coagulation and chlorination) with capacity of 50 cubic meters/day. The secondary effluent is then filtered using sand filters before entering the ultrafiltration membrane (hollow fiber with 100 kD cutoff filters, AST technology, Israel).

Column experiments: column filter experiments were performed with 100/1, or 50/1 (w/w) mixtures of quartz sand and ODTMA-clay complex (20 cm active layer) in a column of 25 cm length and 5 cm diameter. The bottom of the column was covered by 3 cm layer of quartz sand. Quartz sand was thoroughly washed by distilled water and dried at 105 °C for 24 h. For a mixture of 50/1 ratio the column was filled with 650 g sand mixed with 13 g micelle-clay complex, which contained 4 g of ODTMA. Solutions of UF-hollow fiber permeate were passed through the column at a flow rate of (1) 1.2 mL/min, or (2) 50 mL/min. COD, BOD, TSS, EC, turbidity and microbial counts were measured for the initial solution and in each collected fraction of 100 mL in case (1), and after 1, 4, 9, and 14 L in case (2). Each measurement was repeated three times and their average and standard deviation were evaluated.

3. Results and Discussion

3.1 Filtration at Low Flow Rates

The results in Figs. 1-5 show the effect of filtration on several parameters, which characterize the tertiary treated wastewater after the HF ultrafiltration.

The results in Fig. 1 demonstrate for all collected fractions a very significant reduction in total suspended solids (TSS) from an initial value of 6 ppm to a final value of 0 (within the sensitivity of the measurements). In accordance with this outcome, Fig. 1 shows that the turbidity decreased from an initial value of 14 NTU to 0.

Fig. 2 shows a variation of the electrical conductivity (EC) from an initial value of about 1200 μS/cm. For the first 100 mL emerging from the filter the value of EC increased to 1550 μS/cm, but then it kept decreasing on the average to a value below 950 μS/cm for fraction # 20, i.e., after 2 L. The

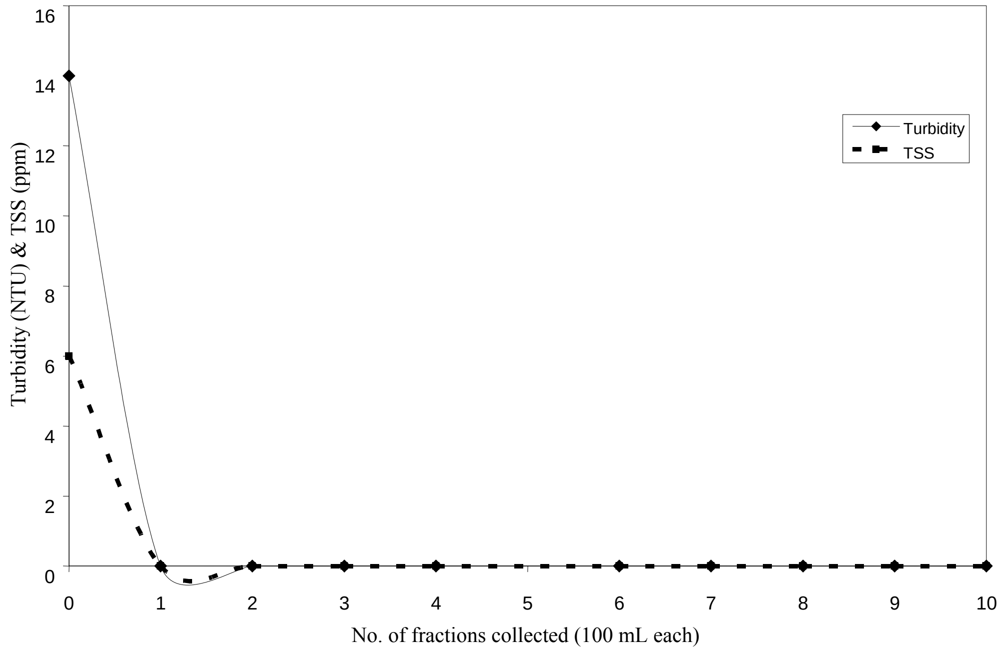

Fig. 1 Variation of total suspended solids (TSS), and turbidity in different fractions collected from clay-micelle-sand column. The mobile phase was tertiary treated wastewater with HF ultrafiltration. The clay-micelle sand ratio was 1 to 50. The flow rate was 1.2 mL/min at room temperature. The volume of each fraction was 100 mL.

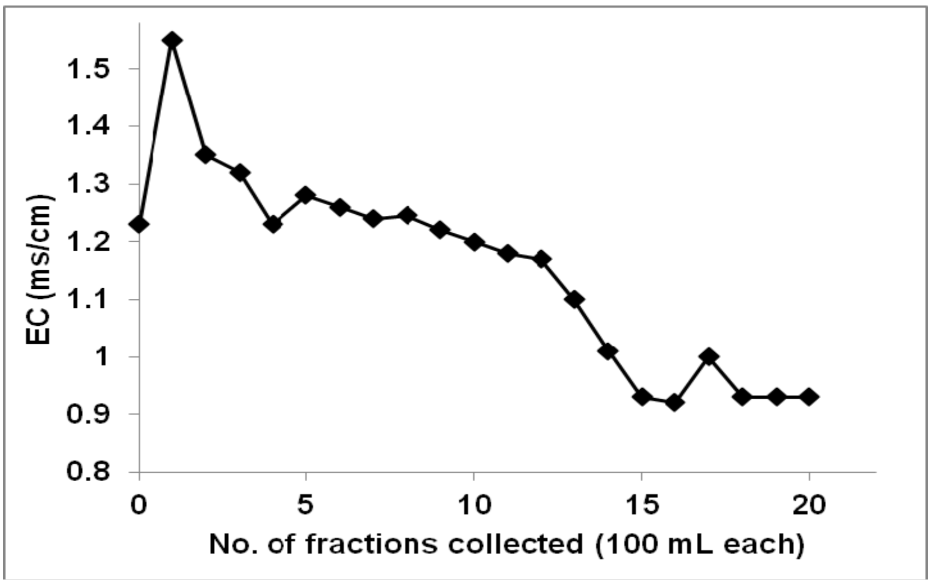

Fig. 2 Variation of electrical conductivity (EC) in different fractions collected from clay-micelle-sand column. Conditions as in Fig. 1. The volume of each fraction was 100 mL.

interpretation of this result is that initially electrolytes released from the filter material contributed to an elevation of the EC, but filtration, which removed components from the solution, caused reduction in the EC. The reduction in EC from the initial value is overall not dramatic, amounting to about 25%.

Fig. 3 demonstrates that filtration by the micelle-clay column of the tertiary treated wastewater after the HF ultrafiltration resulted in a dramatic reduction in the total bacterial count as defined by colony forming units (cfu) per mL. No colonies were formed for the samples after 300, 400, 900 and 1,000 mL, whereas a small number of colonies were detected for several of the samples.

The results in Figs. 1 and 3 indicate that filtration of the tertiary treated water by the micelle-clay complex mixed with excess sand reduced significantly the load of total suspended solids and total bacterial count. The results in Fig. 4 are in a sense more dramatic since they revealed that for all the filtered samples the number of fecal coliforms and total coliforms, which are pathogenic indicators, was reduced to 0.

The results of Fig. 5 illustrate the effect of filtration by the micelle-clay-sand column on the values of COD and BOD. The general trend is that as filtration proceeds there is a dramatic reduction in both COD and BOD values. A tentative explanation for the fact that overall the percents reduction of COD and BOD were increased with sample numbers from 1 to 7 might be due to some channeling, which could occur in the filter, which gradually was reduced. The initial relatively high values of COD and BOD may be due to residues of chemicals in the waste water from laboratories, which were not well removed by the secondary biological treatment.

3.2 Filtration at Intermediate Flow Rates

In this experiment we employed a duplicate system, each consisting of two filters in series. The filters included a micelle- clay complex mixed with excess

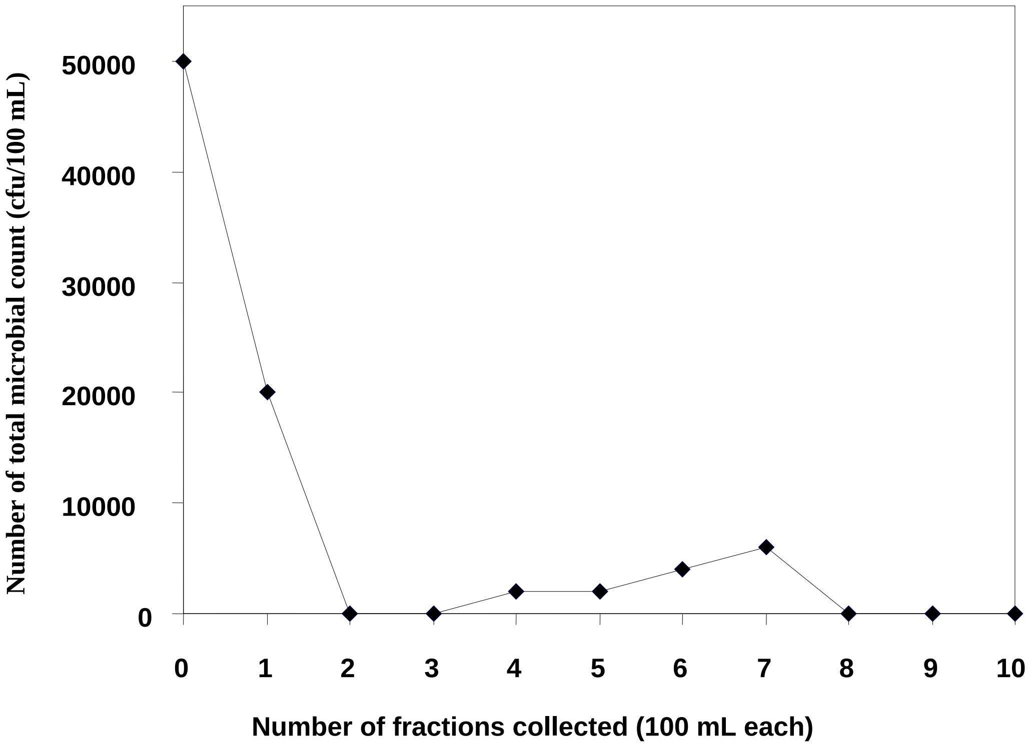

Fig. 3 Variation of total bacterial count in different emerging fractions collected from the clay-micelle-sand column. Conditions as in Fig. 1.

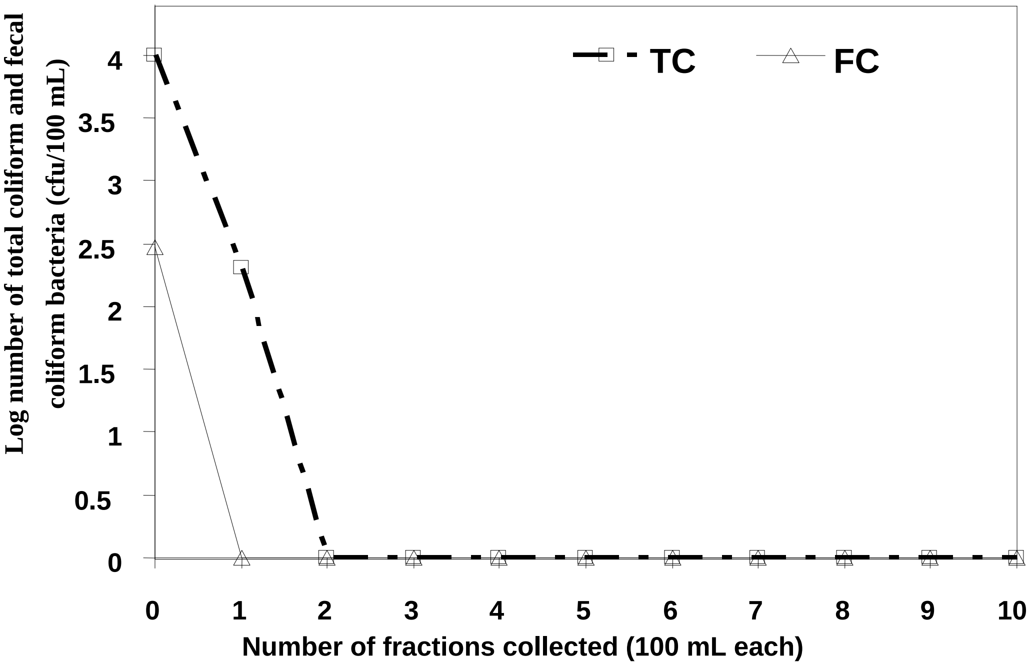

Fig. 4 Variation of total coliform and fecal coliform bacteria in different fractions emerging from the clay-micelle-sand column. Conditions as in Fig. 1.

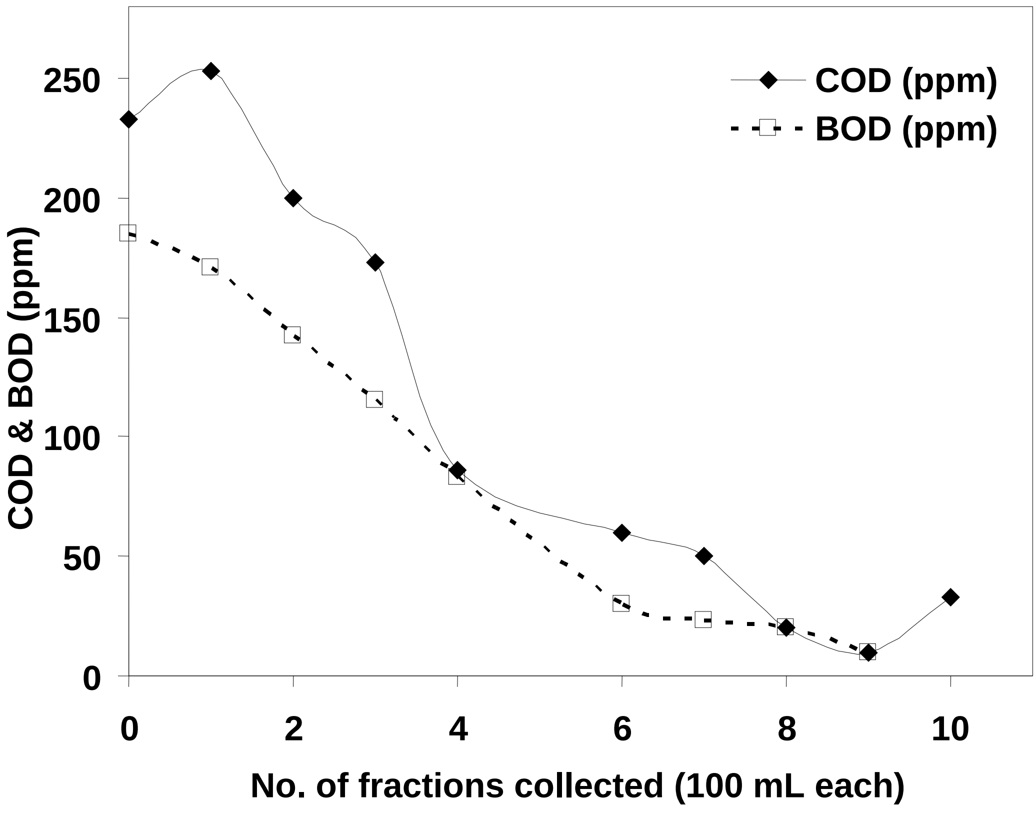

Fig. 5 Variation of the chemical oxygen demand (COD), and biological oxygen demand (BOD) in different fractions collected from clay-micelle-sand column. Conditions as in Fig. 1.

sand (1:100, w/w). The flow rate was 50 mL/min, i.e., 40-fold larger than in the experiments whose results are shown in Figs. 1-5. Possible channeling was largely eliminated by first saturating the filter by slow upward flow. The outcome of this larger scale experiment is shown in Tables 1 and 2. In addition, we report that the values of the pH were varied from 7.7 ± 0.2 in the inlet to 8 ± 0.2 after filtration. The values of the electrical conductivity were in the range of the values shown in Fig. 2, between 1180 and 1235 ± 6 µS/cm.

The turbidity (Table 1) was reduced by an order of magnitude for the water emerging from the second filter up to the passage of 9 L, whereas after 14 L the reduction was marginal. The first column was found slightly efficient in the reduction of the turbidity values by eluting up to 4 L, but was found not efficient at 9 L and 14 L fractions. The values of TSS were reduced more sharply than those of the turbidity in the second column, yielding complete removal after 9 L while the first column showed no efficiency after the passage of 9 L.

The results in Table 2 demonstrate that filtration by the micelle-clay complex reduced dramatically the number of the pathogenic bacteria, fecal coliforms (FC) from an initial value of 50,000 cfu/100 mL to 0 in the water emerging from the second filter after 14 L, whereas for the first filter the corresponding number was 4. It should be noted that this reduction of pathogenic bacteria is without any disinfection. Thus, any chlorinated by-products are eliminated from such treatment. Furthermore, the effluent's bacterial characteristics are in accordance with the WHO guidelines for non restricted irrigations [21]. We also have unpublished results (Abid Nasser and Shlomo Nir) that the micelle-clay complex is quite effective in the removal of several tested viruses and cryptosporidium from water. For the indicator bacteria (TC), the removal by the second filter was complete and by the first filter the decrease was by 4 orders of magnitude. For total bacterial count (TPC) the reduction was by two orders of magnitude after 1 L and by one order of magnitude after 14 L. A flow rate of 50 mL/min corresponds to a flow velocity of 2.55 cm/min, or 1.5 m/h, but theoretical considerations and our experience have shown that the outcome for such a flow velocity for a filter of 40 cm in length and filled with the complex at a 1:100 ratio would correspond to filtration at a flow velocity of more than 10 m/h for a filter filled with complex at a 1:19 ratio and a length of 110 cm. Furthermore, in the case of the longer filter the capacity, i.e., the volume which can be filtered and

Table 1 Values of TSS, turbidity, COD and BOD of wastewater after filtration at a flow rate of 50 mL/min by two columns in series which included a micelle-clay complex mixed with excess sand (1:100, w/w) [a].

Volume (L)	TSS (ppm)	Turbidity (NTU)	COD (ppm)	BOD (ppm)
Inlet	7 ± 0.2	14 ± 1	80 ± 2.0	53 ± 2.0
1	0.5 (2.2) ± 0.1	3.5 (6.5) ± 1.0	33.5 (46.0) ± 4.0	26.0 (45.0) ± 2.0
4	0.0 (4.5) ± 0.1	2.0 (9.0) ± 1.0	22.5 (26.5) ± 4.0	18.0 (20.5) ± 2.0
9	0.0 (7.5) ± 0.1	5.0 (17.5) ± 1.0	16.0 (36.0) ± 4.0	24.0 (33) ± 2.0
14	2.3 (8.2) ± 0.1	13.0 (21.5) ± 1.0	20.5 (25.0) ± 4.0	13.0 (12.5) ± 1.0

[a] Values in parenthesis refer to first column. Results are average values from two systems in duplicate.

Table 2 Microbial removal (FC, TC, and TPC) in colony forming unit (cfu) per 100 mL of wastewater after filtration at a flow rate of 50 mL/min by two columns in series, which included micelle-clay complex mixed with excess sand (1:100, w/w)[a].

Volume (L)	FC per 100 mL	TC per 100 mL	TPC per 100 mL
Inlet	50,000	70,000	300,000
1	0 (0)	0 (0)	1000 (2750)
9	0 (1)	1 (2)	2000 (22,000)
14	0 (4)	0 (5)	39,000 (70,700)

[a] Values in parenthesis refer to first column. Results are average values from two systems in duplicate.

yield the same percent of removal per amount of active component in the filter may be doubled.

The results in Figs. 1-5 and Tables 1 and 2 point out that the incorporation of a filter which includes the micelle-clay complex as a component in the overall system of waste water purification can be useful. It is of interest to note that the UF hollow fiber filter reduced 90-99% of the inoculated bacteria (of an initial value of 100 million per mL), whereas the spiral wound UF membrane reduced their number by 3-4 logs after the reduction by the hollow fiber (Jehad Abbadi, unpublished results). Based on these results, it follows that more experiments at a larger scale should be undertaken, in order to give estimates for the optimal economical planning of the treatment of such waste water.

4. Conclusions

The results indicate that the incorporation of a filter filled with a mixture of a micelle-clay complex in a sequence of purification steps, which include a biological treatment followed by a treatment by a hollow fiber UF with a cutoff of 100 kD, is advantageous in achieving higher quality of treated water. Due to the characteristics of the micelle-clay complex, which has large surface area, net positive charge and large hydrophobic domains, the complex is quite powerful in removing from water pathogenic bacteria, such as fecal coliforms. In addition, it also contributes to other criteria for water purification, such as reduction of TSS, turbidity, COD and BOD. A larger scale experiment involving employment of the micelle-clay in filtration together with other components of the sewage treatment system may elucidate the best economical combination of treatment elements for a safe utilization of treated water for irrigation.

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